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(FILE 'HOME' ENTERED AT 14:11:21 ON 07 DEC 2004)

FILE 'REGISTRY' ENTERED AT 14:11:40 ON 07 DEC 2004
L1 1 S 492-37-5

FILE 'CAPLUS' ENTERED AT 14:12:15 ON 07 DEC 2004

L2 227 S 492-37-5/PREP
L3 91 S 492-37-5/PROC
L4 5 S 492-37-5/PUR
L5 318 S L2 OR L3 OR L4
L6 93287 S ARYL ALCOHOL OR PHENYLALCOHOL OR PHENYL HALIDE OR OLEFIN
L7 9 S L5 AND L6
L8 450185 S ALCOHOL OR HALIDE OR OLEFIN
L9 39 S L5 AND L8
L10 39 S L7 OR L9
L11 31 S L10 AND PY<2000
L12 10 S L11 AND PALLADIUM

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L12 ANSWER 1 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1999:606682 CAPLUS
DOCUMENT NUMBER: 131:336794
TITLE: Highly efficient catalyst system for the synthesis of
2-arylpropionic acids by carbonylation
AUTHOR(S): Seayad, A.; Jayasree, S.; Chaudhari, R. V.
CORPORATE SOURCE: Homogeneous Catalysis Division, National Chemical
Laboratory, Pune, 411008, India
SOURCE: Catalysis Letters (1999), 61(1,2), 99-103
CODEN: CALEER; ISSN: 1011-372X
PUBLISHER: Baltzer Science Publishers
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 131:336794

AB Carbonylation of 1-(4-isobutylphenyl)ethanol has been studied using a
homogeneous catalyst system consisting of PdCl₂(PPh₃)₂/TsOH/LiCl. Higher
reaction rates with TOF up to 1200 h⁻¹ and ibuprofen selectivity >95% have
been achieved at 388 K under a CO partial pressure of 5.4 MPa. The
reaction proceeds through the formation of 4-isobutylstyrene and
1-(4-isobutylphenyl)ethyl chloride as intermediates. The same catalyst
system is shown to be effective for carbonylation of various
 α -arylethanol, vinyl aroms. and corresponding chloro derivs.

IT 492-37-5P

RL: SPN (Synthetic preparation); PREP (Preparation)
(catalytic carbonylation of (isobutylphenyl)ethanol and related
comps.)

RN 492-37-5 CAPLUS

CN Benzeneacetic acid, α -methyl- (9CI) (CA INDEX NAME)

Ph

Me-CH-CO₂H

REFERENCE COUNT: 9 THERE ARE 9 CITED REFERENCES AVAILABLE FOR THIS
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L12 ANSWER 2 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN

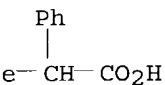
ACCESSION NUMBER: 1999:15905 CAPLUS
DOCUMENT NUMBER: 130:124742
TITLE: Regioselective effect of CoCl₂ in olefin
hydrocarboxylation catalyzed by PdCl₂(Ph₃P)₂ complex
AUTHOR(S): Kron, T. E.; Terekhova, M. I.; Noskov, Yu. G.; Petrov,
E. S.
CORPORATE SOURCE: Nauchno-Issled. Fiz.-Khim. Inst. im. L.Ya. Karpova,
Gos. Nauchn. Tsentr Ross. Fed., Moscow, Russia
SOURCE: Zhurnal Fizicheskoi Khimii (1998), 72(10),
1834-1838
CODEN: ZFKHA9; ISSN: 0044-4537
PUBLISHER: MAIK Nauka
DOCUMENT TYPE: Journal
LANGUAGE: Russian

AB Various factors such as CO pressure, water concentration, excess ligand L (PPh₃),
and the presence of CoCl₂ were examined for their influence on the
regioselectivity of PdCl₂L₂-catalyzed hydrocarboxylation of 1-heptene,
where regioselectivity $S = 100 + r_1/(r_1 + r_2)$ was defined in terms
of the rates of accumulation of normal and branched isomers r_1 and r_2 ,
resp. The bimetallic catalyst system led to an increase in S (from e.g.,
66% without Co 79% with); this was observed even more dramatically with
styrene, where an inversion in was was observed (from 23% without to 57%
with). CoCl₂ itself did not catalyze the hydrocarboxylation reaction.
The synergistic mechanism was discussed.

IT 492-37-5P, 2-Phenylpropanoic acid

RL: SPN (Synthetic preparation); PREP (Preparation)
(effect of CoCl₂ and other reaction conditions on the regiochem. of

olefin hydrocarboxylation catalyzed by PdCl₂(Ph₃P)₂ complex)
N 492-37-5 CAPLUS
N Benzeneacetic acid, α -methyl- (9CI) (CA INDEX NAME)



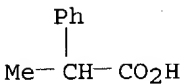
12 ANSWER 3 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN

CESSION NUMBER: 1998:600725 CAPLUS
OCUMENT NUMBER: 129:316015
ITLE: Biphasic Synthesis of 2-Phenylpropionic Acid and Ester
by Interfacial Carbonylation of α -Methylbenzyl
Bromide
UTHOR(S): Norman, Carnley; Wilhite, Benjamin A.; Pham, Duc; Lim,
Phooi K.; Brown, Philip A.
ORPORATE SOURCE: Department of Chemical Engineering, North Carolina
State University, Raleigh, NC, 27695-7905, USA
OURCE: Organic Process Research & Development (1998
, 2(6), 366-378
CODEN: OPRDFK; ISSN: 1083-6160
UBLISHER: American Chemical Society
OCUMENT TYPE: Journal
ANGUAGE: English

B An interfacial synthesis technique was successfully extended to the carbonylation of α -methylbenzyl bromide in an organic-aqueous sodium hydroxide mixture at 35-60 °C and 1 atm using surface-active **palladium**-(4-dimethylaminophenyl)diphenylphosphine complex as the catalyst and dodecyl sodium sulfate as the emulsifier. Depending on the reaction conditions, 2-phenylpropionate in the form of sodium salt and an ester was obtained in 0-83% yield, along with varying amts. of side products that included α -methylbenzyl alc., 2,3-diphenylbutane, di(α -methylbenzyl)ether, and an asym. ether derived from the substrate and an alc. medium. When 2-methyl-1-butanol or 2-ethyl-1-hexanol was used as the organic phase, 2-phenylpropionate ester and sodium salt were obtained in 40-83% yield, with a maximum yield obtained at an optimal aqueous base concentration of about 5 M. At a lower aqueous base concentration,

ore of α -methylbenzyl alc. was formed, whereas at a higher aqueous base concentration, more of 2,3-diphenylbutane and asym. ether were formed. When toluene was used as the organic phase, 2-phenylpropionate salt was obtained in less than 13% yield, and the major side product was α -methylbenzyl alc. at a low aqueous base concentration and 2,3-diphenylbutane at a high aqueous base concentration. In all cases, the formation of 2,3-diphenylbutane was accompanied by a stoichiometric formation of carbonate. The latter implicates the involvement of an oxidative intermediate-tentatively identified as hypobromous acid-that could deactivate the catalyst complex through ligand degradation. Along with the carbonylation reaction, carbon monoxide also underwent a slow, base-induced hydrolysis reaction to form formic acid. With 2-ethyl-1-hexanol as the organic phase, the carbonylation of α -methylbenzyl bromide showed an apparent temperature-dependent activation energy, a first-order dependence each on the substrate, catalyst, and ligand concns. up to the catalyst concentration of 0.0020 M and a ligand:catalyst ratio of 3:1, and a variable-order dependence on the carbon monoxide pressure that switched from first to zero order as the carbon monoxide pressure was increased above 450 mmHg. A reaction mechanism is proposed which yields model rate and yield expressions in accord with the exptl. findings. Results of control expts. with α,α -dibromotoluene in a toluene-aqueous sodium hydroxide mixture indicate that replacement of the α -Me group in α -methylbenzyl bromide by a second bromo group suppressed the formation of substituted benzyl alc. and coupled product. They suggest that the broad product distribution in the carbonylation of α -methylbenzyl bromide relative to the carbonylation of benzyl chloride and α,α -dibromotoluene is attributable to the electron-releasing α -Me group making the substrate susceptible to

hydrolysis and coupling reactions.
 IT **492-37-5P**, 2-Phenylpropionic acid
 RL: SPN (Synthetic preparation); **PREP (Preparation)**
 (biphasic preparation of phenylpropionate via interfacial carbonylation of
 methylbenzyl bromide)
 RN 492-37-5 CAPLUS
 CN Benzeneacetic acid, α -methyl- (9CI) (CA INDEX NAME)



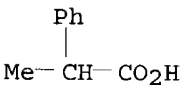
REFERENCE COUNT: 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS
 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L12 ANSWER 4 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1997:594127 CAPLUS
 DOCUMENT NUMBER: 127:277806
 TITLE: Catalytic conversions in water. Part 6. A novel
 biphasic hydrocarboxylation of olefins catalyzed by
palladium TPPTS complexes (TPPTS=P(C₆H₄-m-
 SO₃Na)₃)
 AUTHOR(S): Papadogianakis, Georgios; Verspui, Goran; Maat,
 Leendert; Sheldon, Roger A.
 CORPORATE SOURCE: Laboratory of Organic Chemistry and Catalysis, Delft
 University of Technology, Delft, 2628 BL, Neth.
 SOURCE: Catalysis Letters (1997), 47(1), 43-46
 CODEN: CALEER; ISSN: 1011-372X
 PUBLISHER: Baltzer
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 OTHER SOURCE(S): CASREACT 127:277806

AB Exceptionally high catalytic activities (TOF> 2500h⁻¹) have been achieved
 in the biphasic hydrocarboxylation of propene catalyzed by water-soluble
 Pd/TPPTS complexes. The activity was even higher than that exhibited by
 organic-soluble Pd/PPh₃ systems. This contrasts with the general perception
 that biphasic catalysis normally exhibits lower rates compared to
 analogous reactions in organic media. The hydrocarboxylation of
 4-isobutylstyrene to ibuprofen and of styrene in a two-phase system is
 also reported.

IT **492-37-5P**
 RL: SPN (Synthetic preparation); **PREP (Preparation)**
 (biphasic hydrocarboxylation of olefins catalyzed by **palladium**
 TPPTS complexes)
 RN 492-37-5 CAPLUS
 CN Benzeneacetic acid, α -methyl- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 15 THERE ARE 15 CITED REFERENCES AVAILABLE FOR THIS
 RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L12 ANSWER 5 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1996:469962 CAPLUS
 DOCUMENT NUMBER: 125:142279
 TITLE: Preparation of arylacetic and arylpropionic acids
 INVENTOR(S): Sheldon, Roger A.; Maat, Leendert; Papadogianakis,
 Georgios
 PATENT ASSIGNEE(S): Hoechst Celanese Corp., USA
 SOURCE: U.S., 6 pp.
 CODEN: USXXAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5536874	A	19960716	US 1994-347027	19941130 <--
WO 9626177	A1	19960829	WO 1995-US14578	19951109 <--

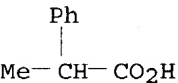
W: ES, GB, JP
RW: AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE
PRIORITY APPLN. INFO.: US 1994-347027 19941130

OTHER SOURCE(S): CASREACT 125:142279; MARPAT 125:142279

AB The title compds. R1C(R2)(R3)COOR4 [I; R1 = halo, OH, C1-8 alkyl, etc.; R2, R3 = H, halo, Ph, etc.; R4 = H, C1-8 alkyl, Ph, etc.] were prepared by carbonylation of (substituted) arylcarbinols R1C(R2)(R3)OH in a two-phase system wherein one phase is an aqueous medium which contains (1) a catalyst which is a water-soluble complex consisting essentially of a Group VIII metal and a hydrophilic ligand such as **palladium** complexed with trisulfonated triphenylphosphine, and (2) optionally an acid, and the second phase comprises said arylcarbinol. Thus, carbonylation of 4-fluorobenzyl alc. in the presence of Pd(OAc)2 and Na salt of trisulfonated triphenylphosphine in H2O/PhMe afforded I [R1 = 4-FC6H4; R2 = R3 = R4 = H].

IT **492-37-5P**, 2-Phenylpropionic acid
RL: IMF (Industrial manufacture); SPN (Synthetic preparation); **PREP**
(preparation of arylacetic and arylpropionic acids)

RN 492-37-5 CAPLUS
CN Benzeneacetic acid, α -methyl- (9CI) (CA INDEX NAME)

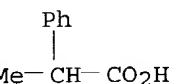


L12 ANSWER 6 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1995:340126 CAPLUS
DOCUMENT NUMBER: 122:314239
TITLE: Carbonylation of styrene and other olefins to keto compounds with cationic **palladium** complexes
AUTHOR(S): Pisano, Carmelina; Consiglio, Giambattista
CORPORATE SOURCE: Swiss Federal Institute of Technology, Department of Industrial Engineering Chemistry, Zurich, CH-8092, Switz.
SOURCE: Gazzetta Chimica Italiana (1994), 124(10), 393-401
CODEN: GCITA9; ISSN: 0016-5603
PUBLISHER: Societa Chimica Italiana
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Various carbonylation reactions, i.e., the synthesis of aldehydes (hydroformylation), of ketones and of alternating copolymers by reaction of olefins with carbon monoxide can be catalyzed by **palladium** complexes of the type PdX2L2 (where L2 = mono- or bidentate phosphorus or nitrogen ligand, X = anion with low coordination ability). The chemoselectivity of the catalytic systems is influenced both by the ligand and by the anion. Analogous nickel complexes are not active for carbonylation under similar reaction conditions whereas platinum complexes catalyze only hydroformylation. Using styrene as the substrate, conditions were found that produce either (E)-1,5-diphenylpent-1-en-3-one or (E)-1,4-diphenylpent-1-en-3-one with high selectivity even in the presence of hydrogen. Furthermore, the influence of various reaction parameters on the activity and on the selectivity for this carbonylation reaction has been investigated. With o-methylstyrene the formation of ketones is less selective than for styrene under the same reaction conditions. With other aromatic substrates such as 2-phenylpropene or (E)-1-phenylpropene only aldehyde formation was achieved. By contrast aliphatic substrates give oligomeric ketones.

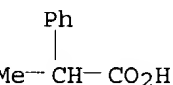
IT 492-37-5P, 2-Phenylpropionic acid
RL: SPN (Synthetic preparation); PREP (Preparation)
(carbonylation of alkenes to carbonyl compds. with cationic
palladium complexes)
RN 492-37-5 CAPLUS
CN Benzeneacetic acid, α -methyl- (9CI) (CA INDEX NAME)



L12 ANSWER 7 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1993:448918 CAPLUS
DOCUMENT NUMBER: 119:48918
TITLE: Regiochemical synthesis of straight chain acids by the
palladium(II) catalyzed hydrocarboxylation of
olefins with oxalic acid
AUTHOR(S): El Ali, Bassam; Alper, Howard
CORPORATE SOURCE: Ottawa-Carleton Chem. Inst., Univ. Ottawa, ON, K1N
6N5, Can.
SOURCE: Journal of Molecular Catalysis (1993),
80(3), 377-81
CODEN: JMCADS; ISSN: 0304-5102
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 119:48918

AB Olefins react with carbon monoxide and oxalic acid, catalyzed by
palladium acetate in the presence of 1,4-
bis(diphenylphosphino)butane, to give linear carboxylic acids
regioselectively. Thus, styrene afforded PhCH₂CH₂CO₂H and PhCHMeCO₂H in a
ratio of 85:15 (86% yield). This process shows excellent functional group
tolerance.

IT 492-37-5P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
RN 492-37-5 CAPLUS
CN Benzeneacetic acid, α -methyl- (9CI) (CA INDEX NAME)

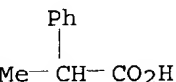


L12 ANSWER 8 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1993:101236 CAPLUS
DOCUMENT NUMBER: 118:101236
TITLE: Formic acid-palladium acetate-1,4-
bis(diphenylphosphino)butane: an effective catalytic
system for regioselective hydrocarboxylation of simple
and functionalized olefins
AUTHOR(S): El Ali, Bassam; Alper, Howard
CORPORATE SOURCE: Ottawa-Carleton Chem., Univ. Ottawa, Ottawa, ON, K1N
6N5, Can.
SOURCE: Journal of Molecular Catalysis (1992),
77(1), 7-13
CODEN: JMCADS; ISSN: 0304-5102
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 118:101236

AB Reaction of mono- and disubstituted olefins, e.g., PhCH:CH₂, with formic
acid, catalytic quantities of palladium acetate and
1,4-bis(diphenylphosphino)butane, in a carbon monoxide atmospheric, affords
carboxylic acids, e.g., PhCH₂CH₂CO₂H, in 45-98% yield. The reaction is
regioselective and, in a number of cases, regiospecific for the

straight-chain acid. Functional groups such as trimethylsilyl, aldehyde, ketone, nitrile, acid and amide and trisubstituted olefins can be tolerated in this reaction.

IT 492-37-5P
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(preparation of)
RN 492-37-5 CAPLUS
CN Benzeneacetic acid, α -methyl- (9CI) (CA INDEX NAME)

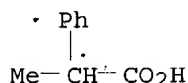


L12 ANSWER 9 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN
ACCESSION NUMBER: 1990:440159 CAPLUS
DOCUMENT NUMBER: 113:40159
TITLE: Carbonylation of arylalkyl halides in preparation of
 α -arylpropionic acids as antiinflammatories
INVENTOR(S): Elango, Varadaraj
PATENT ASSIGNEE(S): Hoechst Celanese Corp., USA
SOURCE: Eur. Pat. Appl., 12 pp.
CODEN: EPXXDW
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 338852	A1	19891025	EP 1989-303995	19890421 <--
EP 338852	B1	19941130		
R: AT, BE, CH, DE, ES, FR, GB, GR, IT, LI, LU, NL, SE				
CA 1338592	A1	19960910	CA 1989-596739	19890414 <--
JP 01311044	A2	19891215	JP 1989-100365	19890421 <--
ES 2065373	T3	19950216	ES 1989-303995	19890421 <--
US 6555704	B1	20030429	US 1995-445593	19950522
PRIORITY APPLN. INFO.:			US 1988-185184	A 19880422
			US 1990-537865	B1 19900614
			US 1992-834979	B1 19920214
			US 1992-973542	B1 19921109

OTHER SOURCE(S): MARPAT 113:40159
AB ARCHMeCO₂H [Ar = Ph, polynuclear aromatic, optionally substituted by (cyclo)alkyl, alkoxy, phenoxy, halo, oxo]], useful as analgesics, antipyretics, and inflammation inhibitors such as ibuprofen, were prepared by carbonylation of ARCHClMe (I) with CO in a protic acidic aqueous medium containing H⁺ and dissociated halide ions, in the presence of a Pd complex, e.g., PdCl₂(PPh₃)₂ as a catalyst, at 10-225° and 100-5000 psig, with the molar ratio of dissociated ions to I of 0.1-5, preferably 0.2-2.0. I were obtained by haloalkylation of the parent aromatic compds. with a hydrogen halide and an alkylation agent, e.g., MeCHO, (MeO)₂CHMe, etc., in the presence of a Lewis acid. A mixture of MeCHO and Me₂CHCH₂Ph (II) was added dropwise to a mixture of II and ZnCl₂ at $\leq 10^\circ$ over 2 h, HCl was passed through the whole at room temperature during .apprx.2 h, and the stirring continued for 6 h to give I [Ar = 4-(Me₂CHCH₂)C₆H₄] (III). The latter in C₆H₆ containing PhCOMe was heated 4 h at 110° in the presence of PdCl₂(PPh₃)₂, concentrated HCl, and KHSO₄, in an autoclave pressurized with 800 psig CO, to give 72% ibuprofen based on a 99% conversion of III.

IT 492-37-5P
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(preparation of, by carbonylation of arylethyl halides)
RN 492-37-5 CAPLUS
CN Benzeneacetic acid, α -methyl- (9CI) (CA INDEX NAME)



L12 ANSWER 10 OF 10 CAPLUS COPYRIGHT 2004 ACS on STN

ACCESSION NUMBER: 1982:405876 CAPLUS

DOCUMENT NUMBER: 97:5876

TITLE: Selective phase transfer and **palladium**
(0)-catalyzed carbonylation, carbalkoxylation, and
reduction reactions

AUTHOR(S): Alper, Howard; Hashem, Khaled; Heveling, Josef

CORPORATE SOURCE: Dep. Chem., Univ. Ottawa, Ottawa, ON, K1N 9B4, Can.

SOURCE: Organometallics (1982), 1(6), 775-8

CODEN: ORGND7; ISSN: 0276-7333

DOCUMENT TYPE: Journal

LANGUAGE: English

AB (Ph₃P)₄Pd catalyzes the carbonylation of benzylic halides to carboxylic acids using 5 N NaOH and CH₂Cl₂ at room temperature and 1 atmospheric. Although the presence of (C₆H₁₃)₄N⁺ HSO₄⁻ (a phase-transfer catalyst) improves the yield, a quaternary ammonium salt is not necessary in these reactions. Reduction (and coupling) of halides occurs using [(PhCH:CH)₂CO]₂Pd as the catalyst under phase-transfer conditions (no reaction takes place in the absence of the phase-transfer catalyst). Esters were obtained by the phase-transfer-catalyzed carbonylation of halides in the presence of (Ph₂PCH₂CH₂PPh₂)₂Pd, while acids were the principal products in the absence of the quaternary ammonium salt.

IT 492-37-5P

RL: SPN (Synthetic preparation); **PREP (Preparation)**
(preparation of)

RN 492-37-5 CAPLUS

CN Benzeneacetic acid, α-methyl- (9CI) (CA INDEX NAME)

